

Original citation:

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Epitaxial Templating of C_{60} with a Molecular Monolayer

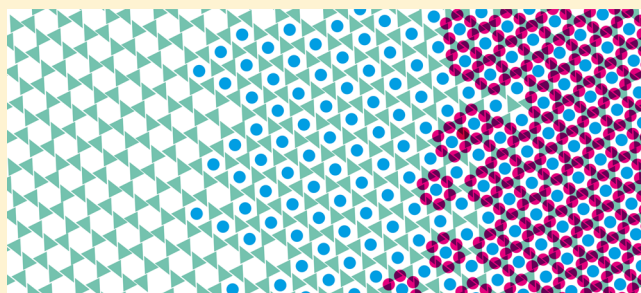
L. A. Rochford,^{*,†} T. S. Jones,[†] and C. B. Nielsen[‡]

[†]Department of Chemistry, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL, United Kingdom

[‡]Materials Research Institute and School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

S Supporting Information

ABSTRACT: Commensurate epitaxial monolayers of truxenone on Cu (111) were employed to template the growth of monolayer and bilayer C_{60} . Through the combination of STM imaging and LEED analysis we have demonstrated that C_{60} forms a commensurate 8×8 overlayer on truxenone/Cu (111). Bilayers of C_{60} retain the 8×8 periodicity of templated monolayers and although Kagome lattice arrangements are observed these are explained with combinations of 8×8 symmetry.



The ability to control the structure of crystalline layers of organic semiconductors is hugely attractive in the field of organic electronics.^{1–4} By modifying the crystal structure of organic materials, structure–property relationships can be exploited for fundamental understanding and device applications.^{3,5} A concerted research effort has been directed into using open-pored low dimensional organic frameworks to control the earliest stages of crystallization in organic semiconductors, most notably buckminsterfullerene (C_{60}) in ultrahigh vacuum and at solid/liquid interfaces.^{6–15} Here we present the use of a commensurate epitaxial template to direct the growth of commensurate epitaxial C_{60} layers. This strategy imparts the structural symmetry and in-plane structural order of the substrate into the molecular template and subsequent C_{60} layers. Our recent work has demonstrated that truxenones, a family of 3-fold symmetric organic semiconductors, self-assemble to form epitaxial open-pored structures on Cu (111), a highly unusual observation in semiconducting organic molecules.^{16,17} Combining truxenone and Cu (111) allows the creation of model surfaces to understand directed assembly behavior while employing a material system that is relevant for high performance device applications such as organic photovoltaics.^{18–20} Through a combination of STM (Scanning tunnelling microscopy) and LEED (Low energy electron diffraction), we demonstrate that a modified C_{60} layer forms within the pores of the truxenone network, exhibiting an 8×8 unit mesh with respect to the underlying Cu(111) surface. A second C_{60} layer is also characterized and corresponds to three additional 8×8 unit meshes laterally translated with respect to the substrate. The combination of fundamental hexagonal symmetry is used to explain ostensibly complex surface symmetry (that of a Kagome lattice). These structural conclusions are unambiguously demonstrated by considering both real space visualization (STM) and reciprocal space structural analysis (LEED).

Our recent work has established that truxenone molecules (Figure 1a inset) form a commensurate 8×8 structure on the Cu (111) surface at room temperature.^{16,17} STM images of small (a) and large (c) areas of the truxenone/Cu (111) evaporated on to clean Cu (111) in ultrahigh vacuum (UHV) [full experimental procedures are present in the Supporting Information] are shown in Figure 1 along with a LEED pattern (b) of the same surface recorded at 13 eV. This arrangement of

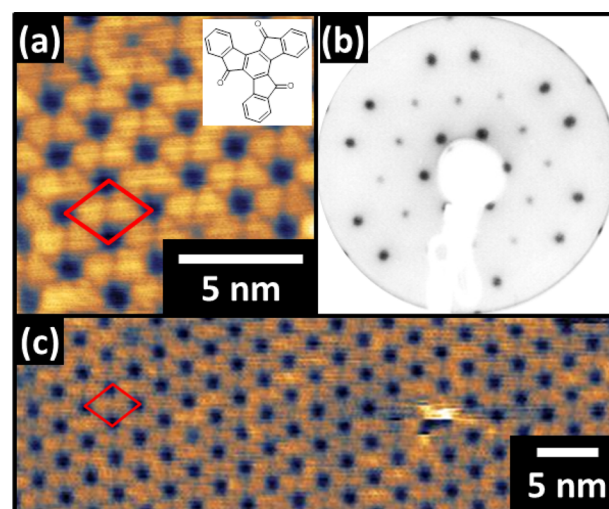


Figure 1. STM images ($V_s = -1.25$ V, $I_t = 65$ pA) of small (a) and large (c) areas of 8×8 truxenone/Cu (111) (unit cells marked by red rhombuses) along with a LEED pattern (b) at 13 eV. The inset in panel a shows the chemical structure of the truxenone molecule.

Received: July 27, 2016

Accepted: August 19, 2016

Published: August 19, 2016

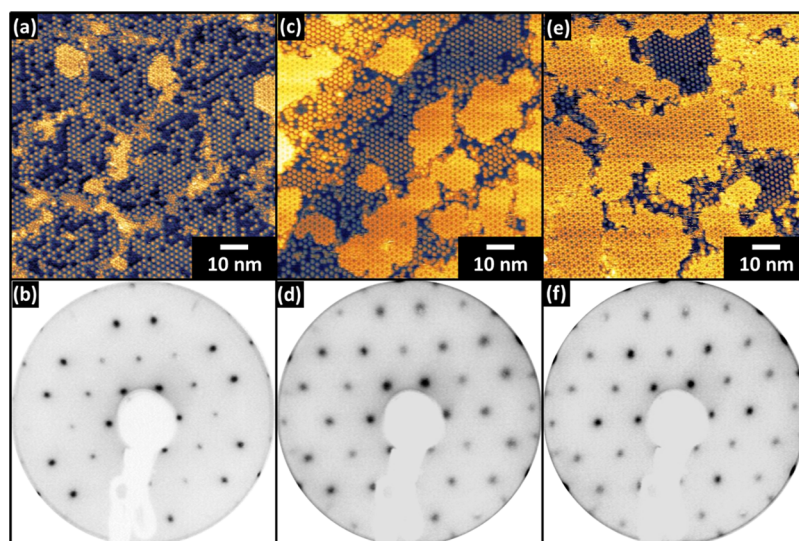


Figure 2. STM images (all $V_s = -1.65$ V, $I_t = 75$ pA) and corresponding LEED patterns (all 13 eV) of low (a, b) medium (c, d) and high (e, f) coverages of C₆₀ on truxenone (8×8)/Cu (111) surfaces.

molecules effectively creates an ordered array of open pores, approximately 0.7 nm in diameter and exactly 2.04 nm apart, aligned with the principal lattice vectors of the substrate.

The pro-chiral nature of truxenone means that surface induced enantiomers are possible when supported by a surface, but these cannot be discriminated between in our experiments.¹⁶ Consequently, no obvious “handedness” is observed in the supramolecular arrangement creating the pores although an achiral surface cannot be established.^{21,22} A proposed packing schematic with potential hydrogen bonds indicated is included in the [Supporting Information](#) (Figure S1).

C₆₀ was sequentially evaporated on to this porous mesh and probed by scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED). The STM image in [Figure 2a](#) demonstrates that C₆₀ molecules form a hexagonal lattice on top of the truxenone layer. Each “pore” of the 8×8 truxenone/Cu (111) mesh accommodates a single C₆₀ molecule, leading to the formation of a C₆₀ layer with the same periodicity as the underlying 8×8 mesh. The LEED pattern from the same surface ([Figure 2b](#)) confirms that 8×8 symmetry is preserved on the addition of C₆₀. As the C₆₀ layer also exhibits 8×8 registry with the underlying Cu (111) the translational and rotation symmetry of the substrate was preserved. In the same STM image ([Figure 2b](#)) brighter islands can be observed which may correspond to bilayer growth of C₆₀. The observation of bilayers was surprising as the first C₆₀ layer is not complete due to a seemingly random distribution of molecular vacancies. Some isolated molecules can be observed (lower middle) along with single molecular vacancies within the C₆₀ domains of the first layer. This is indicative of the stability of individual molecules absorbed in the pores of the truxenone structure and precludes any hierarchical assembly process.²³

To ascertain whether or not bilayer growth was responsible for this observation, additional C₆₀ was added to the surface in two stages. For intermediate coverages ([Figure 2c,d](#)), where the growth time was doubled, the areas of brighter contrast were more abundant and coexisted with monolayer regions. At higher coverage ([Figure 2e,f](#)), where the growth time was quadrupled, the brighter areas accounted for approximately 90% of the surface although monolayer regions were still observed. This strongly suggests that the assertion that these

regions are bilayers of C₆₀ is correct, and indicates that bilayer formation was observed even without completion of the first C₆₀ layer. Observation of this kind of growth indicates that adsorption of C₆₀ onto the truxenone template and the first layer of C₆₀ molecules is similarly energetically preferable.

The second layer of C₆₀ molecules form a Kagome lattice²⁴ structure, something previously observed for C₆₀ and C₇₀ layers on porous molecular layers.²⁵ Although the authors have presented structural and energetic arguments for the formation and stabilization of these structures, we believe that they are simply an expression of the same 8×8 symmetry as the first layer of C₆₀ molecules. On close inspection every molecule in the second layer can be defined by a combination of 8×8 unit meshes. This is demonstrated schematically in [Figure 3](#); panel (a) shows STM of monolayer and bilayer regions in the same area.

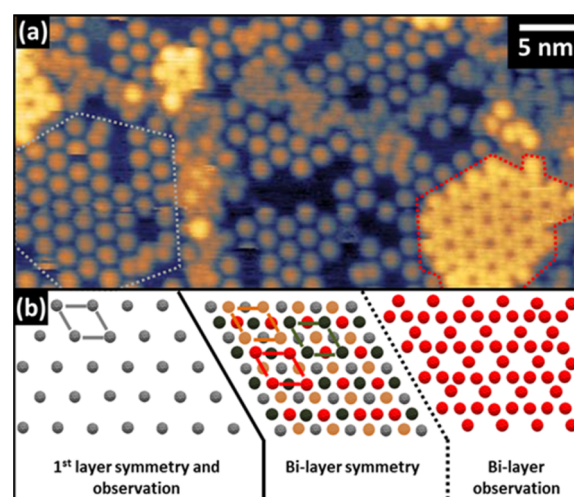


Figure 3. STM image ($V_s = 1.5$ V, $I_t = 65$ pA) (a) of monolayer (white dashed box) and bilayer (red dashed box) regions. Panel (b) demonstrates three individual 8×8 meshes (separately colored, unit cells marked) translated along the gray 8×8 mesh by half a unit cell along each of the primitive lattice directions to create the observed Kagome lattice.

In the left of panel b the symmetry of the first layer is depicted, the unit mesh marked by a gray rhombus. The middle panel shows the close-packed structure created by translating this mesh along each of its primitive translation vectors by half a unit cell length. If the underlying (first C_{60} layer) gray mesh is removed (to only consider the second layer) and the remaining three lattices are uniformly colored, a pattern closely matching the observed bilayer visualization is realized. This suggests that the second C_{60} layer is, in fact, a commensurate 8×8 structure despite initially appearing to have more complex symmetry. The observed Kagome lattice is formed by accommodation of three different 8×8 meshes on to a single underlying 8×8 C_{60} layer. A packing schematic considering the underlying truxenone lattice is included in Supporting Information (Figure S3).

These observations may explain the origin of Kagome lattices of C_{60} observed by other authors, but as previous studies did not include LEED data, no direct comparison can be made. Although the periodicity of each LEED pattern is identical (i.e., the unit cell of the C_{60} and truxenone are the same) the intensity of the second and third order beams showed distinct differences. This indicates that although the C_{60} is templated into a lattice with common 8×8 symmetry the surface structure is not the same as the truxenone/Cu (111) 8×8 .

In addition to templating the in-plane structure of the C_{60} layer the growth mode is also modified when compared with C_{60} grown on bare Cu (111). It is well documented in the literature that C_{60} on Cu (111) forms a 4×4 overlayer (confirmed by LEED patterns in Figure S4).^{26,27} STM images (Figure S4) show that C_{60} forms triangular three-dimensional islands on Cu (111) with areas of exposed substrate remaining. The apparent size of C_{60} molecules in each layer of the multilayer structure is similar, and smaller than those in the first layer of the C_{60} /truxenone system.

The larger apparent size of the first layer of templated C_{60} molecules most probably results from geometric factors rather than electronic effects. The apparent lateral size of first layer molecules (approximately 2 nm, Figure S5) is likely increased by convolution of the molecular profile with the STM tip geometry, whereas the apparent size of those in the second (approximately 1 nm Figure S5) layer will be a more accurate representation of the distance between C_{60} molecules. In addition, first layer C_{60} molecules are likely to be mobile within the pores of the truxenone network in which they are captive. The rate of molecular motion is expected to be sufficiently high at room temperature that STM images represent an average of the position, resulting in larger apparent size. In both cases, second layer C_{60} molecules would be expected to appear as smaller features than their first layer counterparts.

Further evidence is present in Figure 3, where C_{60} molecules at the edge of the red-dashed second layer region appear larger than those in the center. Combined with isolated second layer molecules with almost identical apparent heights to molecules in the first layer, these observations preclude apparent height differences based on electronic effects.

Despite the difference in appearance the periodicity of first and second layers was identical as demonstrated by LEED patterns. These results demonstrate that epitaxial organic layers can be used to direct the epitaxial growth of multilayers of C_{60} . The formation of Kagome lattices is also observed in bilayers, and justified by the formation of multiple 8×8 lattices in the bilayer structures. The application of complementary surface

imaging and diffraction allows the simple symmetry underlying complex visualizations to be revealed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b01656.

Full experimental details, molecular packing schematics, STM images, and LEED patterns of C_{60} on Cu (111). (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: luke.rochford@warwick.ac.uk.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge support from the Engineering and Physical Sciences Research Council [Grant Number EP/H021388/1]. The raw data associated with this article can be accessed at the following: DOI:10.17632/gm2mfj3xd.1.

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